Perspective

The Impact of Shale Gas in the Chemical Industry

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Introduction

The lower alkanes (methane, ethane, propane, etc.) are very useful as both clean fuels and as basic chemical feedstocks. As such they command an economic premium compared with other choices such as oil and coal. From time to time limited supply has constrained demand but also encouraged development of alternative chemistries and feedstocks. The development of new production technologies for unconventional gas sources in shale formations has significantly increased potentially available supply, fundamentally altered economics, changed demand patterns, and multiplied the ways both traditional and alternative chemistries might be exploited. The purpose of this article is to outline how natural gas became useful as both a fuel and feedstock, how limited supplies and government regulations lead to shifts in demand patterns, to the development of alternative chemistries and catalysts, and to the development of shale gas resources, and finally the impact new shale gas might have specifically on the chemical industry.

Natural Gas

Natural gas is a fossil fuel formed from buried layers of organic biomass exposed to intense heat and pressure over millions of years. It consists mostly of methane sometimes with varying amounts of heavier alkanes, carbon dioxide, nitrogen, helium, hydrogen sulfide, and water. Methane can also be made by methanogenic organisms in marshes, wetlands, rice fields, landfills, and ruminant animals. Natural gas emanating from formations exposed by erosion in seeps or springs has been collected and used for fuel for more than 2,500 years. By the 19th century, natural gas associated with coal (coal bed methane) and with oil production (associated gas) was considered a nuisance and was either ventilated, flared, or collected for fuel by customers served by local distribution pipelines. One such early customer was the glass production industry which particularly benefited from cleaner-burning fuels and therefore tended to be sited near sources of natural gas (for example in Ohio, Pennsylvania, and West Virginia).

Natural gas is also found in geological formations not associated with crude oil (unassociated gas). Natural gas with significant amounts of higher alkanes which can range from ethane up to pentane is considered “wet”. Natural gas with higher concentrations of acid gases such as carbon monoxide and hydrogen sulfide is considered "sour". Natural gas introduced into distribution pipelines is generally first dehydrated, stripped of carbon dioxide and hydrogen sulfide (sweetened), and stripped of higher alkanes (collectively called condensate) to produce a fairly pure methane stream of uniform heating value. Table 1 shows the countries with the largest known methane sources. Russia, Iran, Qatar, Saudi Arabia, USA, and Turkmenistan together account for two-thirds of all conventional natural gas reserves in the world.[1]

In urban areas of the US and elsewhere where many customers could be economically served by transmission and distribution pipelines, natural gas became the dominant fuel for heating and cooking, especially after 1950. In rural areas with lower population density, customers were served by easily liquefied propane and butane derived from natural gas condensate and delivered by tanker truck. Condensate ethane, which is difficult to liquefy but also undesirable in cooking fuel because of possible soot deposition, was either used as local industrial fuel or reinjected into hydrocarbon formations to help maintain reservoir pressure. Methane also saw use as a chemical feedstock for synthesis gas (syngas, a mixture of carbon monoxide and hydrogen) via steam reforming technology, for example for ammonia and methanol production, replacing previously employed coal and coke gasification. Methane also replaced coal-derived water gas in the chemical industry as a gaseous fuel for high temperature furnaces in which tube impingement erosion was a consideration, such as in ketene production by acetic acid cracking.

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Table 1. Estimated Proved Reserves of Natural Gas

Rank	Country	Proved reserves (billion cubic feet), Jan 1, 2012	Proved reserves (billion cubic feet), Jan 1, 2011	Proved reserves (billion cubic feet), Jan 1, 2010	Share of total, Jan 1, 2012
1.	Russia	1,680,000	1,680,000	1,680,000	24.9%
2.	Iran*	1,680,000	1,045,670	1,045,670	17.3%
3.	Qatar*	890,000	895,800	899,325	13.2%
4.	Saudi Arabia*	283,000	275,200	263,000	4.2%
5.	United States	272,509	244,656	244,656	4.0%
6.	Turkmenistan	265,000	265,000	265,000	3.9%
7.	United Arab Emirates*	215,035	227,900	214,400	3.2%
8.	Venezuela*	195,100	178,860	175,970	2.9%
9.	Nigeria*	180,458	186,880	185,280	2.7%
10.	Algeria*	159,000	159,000	159,000	2.4%
11.	Indonesia	141,060	106,000	106,000	2.1%
12.	Iraq*	111,520	111,940	111,940	1.7%
13.	China	107,000	107,000	107,000	1.6%
14.	Kazakhstan	85,000	85,000	85,000	1.3%
15.	Malaysia	83,000	83,000	83.000	1.2%
World total		6,746,751	6,647,341	6,609,346	100.0%
Total OPEC**		3,330,137	3,211,152	3,182,829	49.4%

Data Source: US Energy Information Administration

Ethane as a Chemical Industry Feedstock

A fundamental change in the chemical industry occurred when steam cracking technology developed to reduce the molecular weight of petroleum fractions was applied to the thermal dehydrogenation of ethane to produce ethylene (and hydrogen).[2] Previously, the ethane had been generally considered a natural gas waste product with only limited fuel applications. That changed dramatically as ethylene became the principal building block for many families of addition polymers (polyethylene, polystyrene, poly(vinyl chloride), polyvinylacetate, etc.) as well as a number of chemical intermediates (acetaldehyde, ethylene oxide, ethylene glycol, ethanol, ethyl ether, etc.). The same cracking technology was also applied to heavier natural gas condensate components including propane and butane producing propylene and butadiene leading to polypropylene, polyacrylates, polymethacrylates, polycarbonates, and important intermediates like acetone, phenol, isopropyl alcohol, and many, many more. These polymers and intermediates led to huge growth in the chemical industry and to an era of materials substitution especially of polymers for natural fibers, metals, glass, wood, etc. that persists to this day. These same chemicals can be and are produced from olefins derived from cracking light petroleum naphtha fractions from crude oil refineries especially in regions where natural gas condensate is not readily available, but those with access to condensate generally enjoyed an economic advantage.[3]

In the commodity organic chemicals sector, carbon-carbon combination reactions are relatively rare with the notable exceptions of aldol condensation reactions among aldehydes and ketones, alkylation reactions, and addition polymerizations. Therefore, one-carbon-molecule compounds like methanol, formaldehyde, formic acid, methylene chloride, etc. tended to be derived from one-carbon (C_1) methane or carbon monoxide (itself derived from methane), two-carbon compounds (ethylene, acetaldehyde, ethanol, acetic acid, ketene, ethylene glycol, etc.) from two-carbon (C_2) ethane, three-carbon compounds (propylene, acetone, isopropyl alcohol, acrylic acid, etc.) from C_3 propane, and so on as shown in Figure 1. Larger molecules were often formed through reactive functional groups (ethers, esters, amides, etc.) rather than extending or combining carbon backbones. Thus methane, ethane, propane, and butane, all obtained from wet natural gas (or light petroleum naphtha), as well as aromatics largely obtained by catalytic reforming of medium naphtha in oil refineries, became the principal basic raw materials of the modern organic chemicals industry.

From time to time, supply and other economic disruptions and catalysis innovations triggered exploration of alternative feedstocks and chemistries for the basic organic intermediates. For example, during conditions of limited access to petroleum, Fischer-Tropsch synthesis (a form of condensation polymerization) from syngas derived from coal, methane, and even biomass has been used as an alternate route to medium-chain carbon molecules, especially for fuel use.[4] Similarly, in periods of methane shortage or high prices, coal gasification has been used for syngas production rather than the more common methane steam reforming or methane partial oxidation.[5]

Catalyst innovations also have played a major role in feedstock selection. Perhaps one of the most striking examples was the discovery that rhodium can replace cobalt in a number of carbonylation (CO) and hydroformylation or oxo ($H_2 + CO$) reactions (both of which are examples of carbon backbone extension reactions, in these cases by one carbon) allowing operation of these previously known but little practiced reactions at significantly lower pressures and higher yields.[6,7] One of the first commercialization of this advance was the Monsanto process for acetic acid by methanol carbonylation, that is, a two-carbon molecule via a C_1 route.[8] Prior to this, industrial acetic acid had generally been made by the oxidation of acetaldehyde, itself made by oxidation of ethylene, a C_2 route. The new route, enabled by catalysis innovation, proved to be so economically attractive that acetic acid, once a C_2 chemical, became instead a C_1 chemical. This success ultimately lead to the development of related C_1 technologies for such intermediates as methyl acetate, acetic anhydride, ketene, acetaldehyde, and vinyl acetate, all previously C_2 chemicals. Likewise (through oxo synthesis of aldehydes from olefins), three-carbon propionaldehyde,

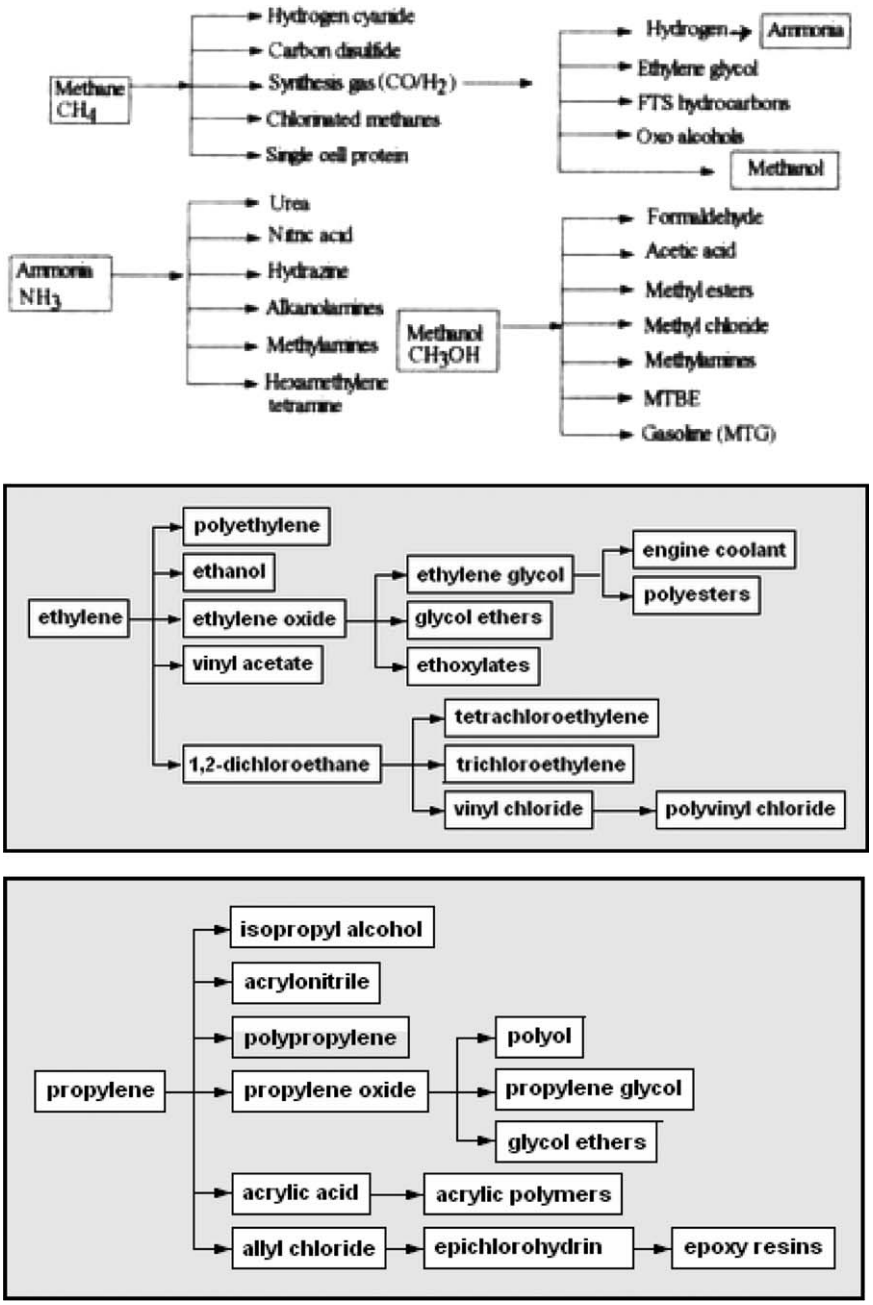


Figure 1. Traditional C_1, C_2, and C_3 production schemes.

Source: HIS GlobalSpec.

propionic acid and normal-propanol all became C_2 chemicals, and normal-butyraldehyde and its derivatives, formerly C_2 chemicals via aldol condensation, became C_3 chemicals, and whole families of derivatives from not previously available iso-butyraldehyde were created. The fact that rhodium is expensive, lead to more catalyst innovations, including examination of iridium, nickel, ruthenium, and other carbonylation and hydroformylation facilitators.[9–11] Although in regions with abundant natural gas condensate C_1, C_2, and C_3 routes all are derived from natural gas components, in other regions with less advantageous access to ethylene and propylene, these innovations opened up routes to formerly C_2 and C_3 chemicals instead from syngas derived from dry natural gas or coal as shown in Figure 2.[12,13]

Economic Disruption

As shown in Figure 3, natural gas production in the US rose steadily with increased demand in the postwar period until the cost of new production significantly exceeded the federally-controlled wellhead price in the early 1970s. New wells then were not drilled, production leveled, and during

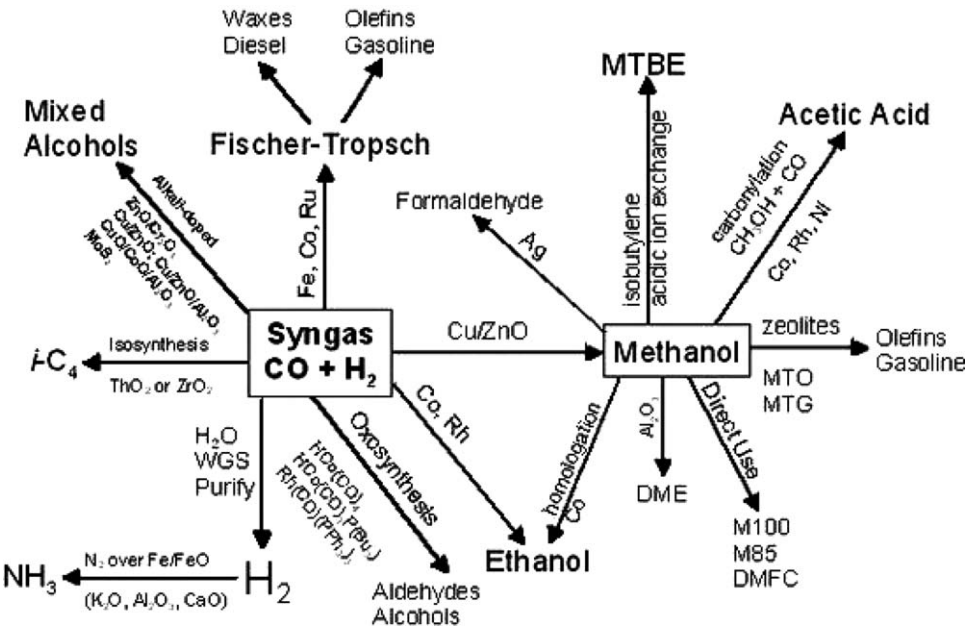


Figure 2. Chemical production from syngas only.

Source: P. L. Spath and D. C. Dayton, preliminary screening - technical and economic assessment of synthesis gas to fuels and chemicals with emphasis on the potential for biomass-derived syngas, National Renewable Energy Laboratory, NREL/TP-510–34929, December, 2003.

the particularly cold winter of 1977 actually failed to meet demand resulting in shortages and curtailments.[14] This situation led some to consider coal gasification as a replacement for natural gas for fuel and chemical feedstock or as the feedstock for synthetic methane (substitute natural gas), and a number of such plants were built.[15,16] Shortages also resulted in a number of new governmental policies, regulations, and deregulations that had various effects including ultimately a higher but fairly stable natural gas price. However, although there were some variations in total demand, supply never significantly exceeded the production rate reached in 1972 which was regained in the mid-1990s and remained nearly constant for the next decade.[17]

However, starting about 1999 in response to new governmental policies, increased demand for natural gas by nonregulated nonutility electric power generators in the United States shown in Figure 4 outstripped natural gas production capacity, which resulted in a supply-demand imbalance and a nearly a quadrupling in gas price.[18] As the increased fuel costs could be partially passed on to these nonregulated electric power customers, natural gas for the power-generation sector began to displace methane previously used in the industrial and especially the highly competitive chemical sectors. Production of some methane derivatives including methanol and ammonia moved off-shore to regions with "stranded" gas not experiencing competition from the electric power sector.[19] However, certain other methane chemicals, especially hydrogen, that were more difficult to transport could not be so easily off-shored, and, therefore, experienced large price increases.[20] Eventually, natural gas prices returned closer to more traditional values as demand was rebalanced with nearly level supply, but with electric power production having displaced many chemicals previously derived from methane.[21] This supply-demand disruption caused some to again reconsider alternative basic feedstocks, particularly coal, petroleum coke, and biomass as sources for hydrogen and C_1 chemicals.[22]

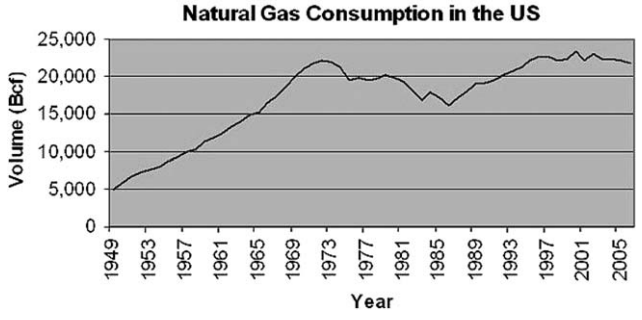


Figure 3. Natural gas production 1950–2005.

Data Source: http://www.eia.gov/dnav/ng/ng_cons_sum_dcu_nus_a.htm.

Since in many cases condensate ethane prices were contractually linked to natural gas prices, this incident also resulted in a more than doubling in ethylene price in the US which affected much of the C_2 chemical chain and decreased or eliminated economic advantages condensate-sourced ethylene enjoyed over naphtha-cracked feedstock.[23] Although in this case there was no actual supply-demand imbalance, this market disruption did increase research interest in C_1 routes to ethylene- and propylene-derived chemicals, triggered a restructuring of much of the commodity polyolefin industry, caused a shift in production of ethylene derivatives to locations that had not experienced ethane price increases (especially to the Persian Gulf), and even consideration of ethylene produced from sugar-derived bioethanol.[24–27]

During this time there was significant discussion of peak-gas analogous to peak-oil, with calls for more methane

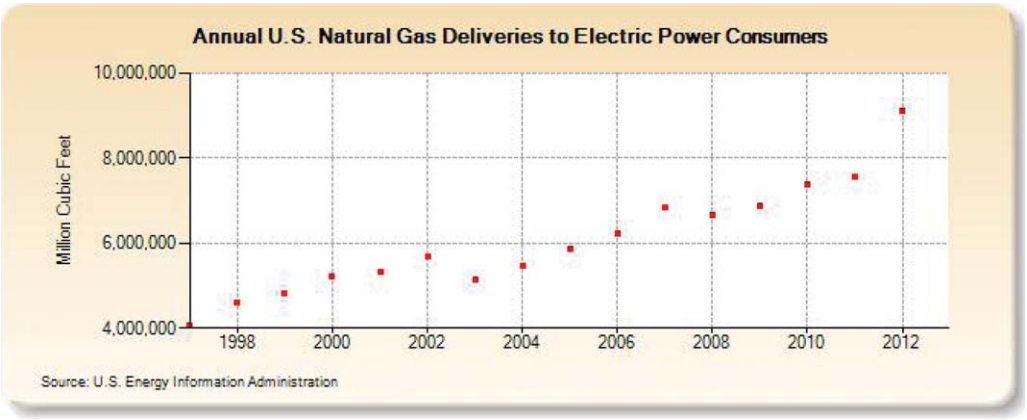


Figure 4. Increased natural gas use for electric power generation.

Source: US Energy Information Administration.

imports including LNG as mechanisms for meeting future demand increases, especially as natural gas and combined-cycle technologies were seen as a more efficient and lower carbon alternatives to coal for electric power generation, and as such a readily implementable first step in climate change mitigation.[28,29] Natural-gas-fired turbines also served as spinning reserve backup for time-variant wind power, another developing element of climate change mitigation.[30]

Shale Gas

Changing natural gas consumption patterns and projected demand growth also spurred interest on the production side. Of particular attention were gas-containing shale formations which were long known but considered an unconventional resource and not counted among reserves because wells previously drilled through these low-permeability strata resulted in very little production despite their fairly high-hydrocarbon content. However, natural gas had been produced in small quantities from naturally fractured shale formations since 1821.[31] The breakthrough came from the application of directional (horizontal) drilling, hydraulic fracturing, and microseismic monitoring technologies (Figure 5), all previously developed for particular oil field situations, to hydrocarbon-containing shales encouraged by a number of government-sponsored research programs, technology demonstrations, and tax credits.[32–35] It was found that marine-deposited shales with higher brittle mineral content would respond favorably to hydraulic fracturing while nonmarine shales containing more ductile clay did not.[36]

After much technology refinement, the first economically commercial shale gas was produced by Mitchell Energy in

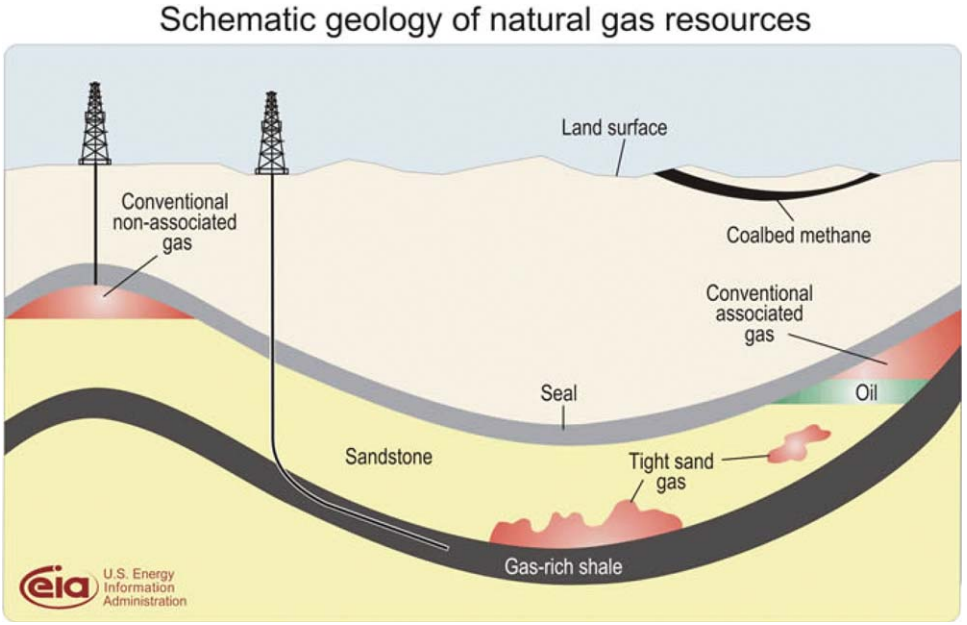
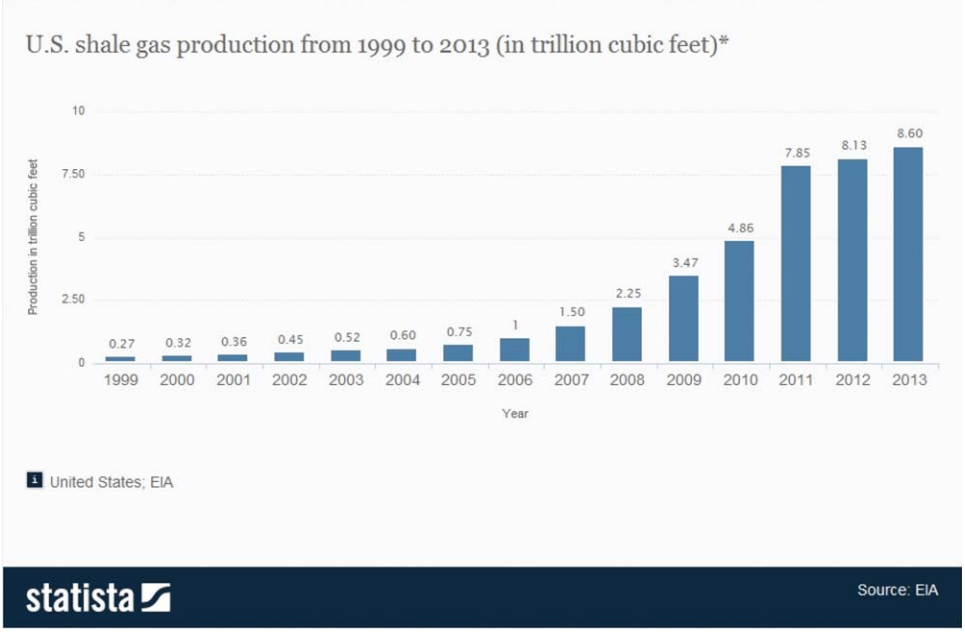


Figure 5. Shale gas extraction schematic.

Source: US Energy Information Administration.

Table 2. US Shale Gas Production 1999–2013



Source: US Energy Information Administration

the Barnett Shale Formation in the Fort Worth Basin in 1998 using slick-water fracturing.[37] Since then shale gas production has risen rapidly in the US (Table 2), reaching 8.6 trillion cubic feet (250 billion cubic meters) in 2013, nearly 35% of all gas production.[38] There are at least 20 shale gas formations in the US (Figure 6) located in most of the hydrocarbon-bearing geologic basins. In 2013 the states of Texas, Louisiana, and Pennsylvania accounted for three-quarters of the total shale gas produced. Recent estimates have placed the total amount of shale gas reserves in the US at 4,600 trillion cubic feet of which 1,200 trillion cubic feet is considered technically recoverable. Shale gas reserves have also been estimated for the rest of the world at 31,100 trillion cubic feet of which perhaps 7,300 trillion cubic feet may be technically recoverable (Table 3). While estimates of reserves of all types change frequently, this is approximately one-half as much as the total worldwide recoverable conventional natural gas.[39] The countries believed to contain the greatest amounts of recoverable shale gas include the USA, China, Argentina, Algeria, Canada, and Mexico (Figure 7). The same directional drilling, hydraulic fracturing, and microseismic monitoring technologies have also been applied to tight light oil bearing shales, for example the Bakken formation in North Dakota and the Eagle Ford formation in Texas, with similar dramatic results which some believe could lead to the complete elimination of the need for U.S. crude oil imports by 2035.[40]

Since unlike crude oil there does not exist a globally integrated market for natural gas because of the lack of an equivalent distribution infrastructure, the impact of the surge in shale gas production in the US has been a steady decrease in natural gas price compared to the price of crude oil (a ratio that except during supply disruptions had held approximately constant for decades).[41] As seen in Figure 8, this decreasing trend (depicted is a rise in the ratio of oil price to gas price) started in 2004 and significantly accelerated after 2008 as shale gas production became a more significant portion of all natural gas. This was so even as total natural gas consumption increased nearly 25% to record high levels largely as a result of the continuing displacement of coal for electric power generation, increased methane feedstock demand resulting from the restart of previously shuttered and newly constructed methanol and ammonia plants, and generally improving economic conditions.[42] Natural gas prices hit a relative low in early 2012, but recovered somewhat since then as shale gas production discipline helps keep supply in closer balance with ever increasing demand. Nevertheless, shale gas appears a less expensive alternative to meet incremental demand and natural gas price compared to crude oil remains about one-third its previous long-term value.

Shale Gas Condensate

The earliest shale gas production from the eastern Barnett Formation was fairly dry and did not immediately attract the attention of the chemical industry. However, later developed fields proved to be quite wet, some containing as much as 20% or more condensate.[43] In regions with existing condensate processing infrastructure, shale gas production added significantly to condensate availability and once again improved the economics of condensate crackers and the C_2 and C_3 products made from ethylene and propylene. In regions without much existing condensate processing infrastructure like the large Marcellus Field in the northern Appalachian Basin, shale gas condensate has become an issue.[44] One proposal has been to send excess condensate to Canadian oil sand producers for bitumen and heavy oil dilution for more economic transportation.[45] Another option is to

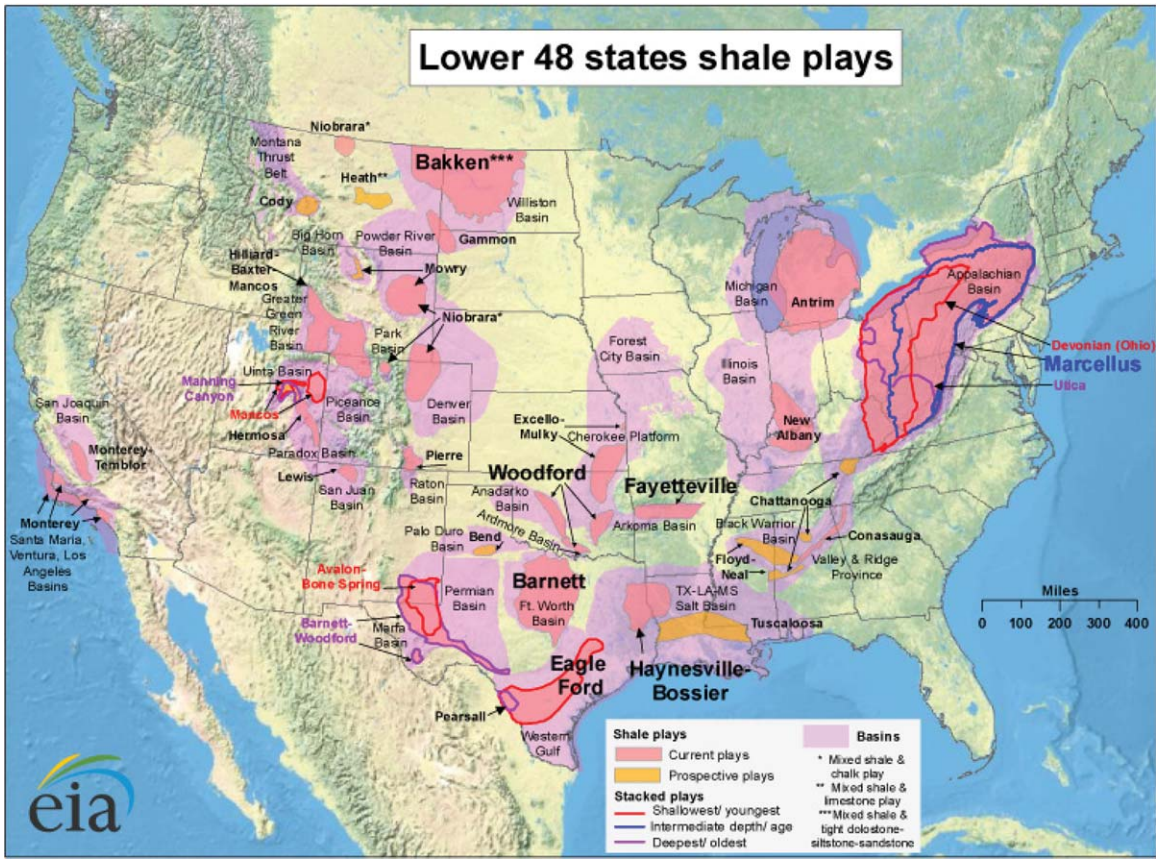


Figure 6. US shale gas and shale oil plays.

Source: US Energy Information Administration.

send condensate to existing ethylene facilities in the Midwest (including Ontario), Louisiana, or Texas.[46] A third option is to construct new condensate processing capacity in these regions in the form of crackers, which then would be accompanied by other new processing units for the production of C_2 and C_3 derivatives such as polyolefins and potentially other intermediates. Plans have been announced to consider these very options in Pennsylvania, West Virginia, and Ohio.[47]

The economics of such a development decision are complex. Factors include the expected long term availability, cost, and composition of shale gas condensate, process technologies and designs selected, product slates chosen, regional markets, transportation and distribution channels, the competitive response from existing producers, etc. Yet, in some locations, excess shale gas condensate may be the initiator for the creation of a new chemical processing industry infrastructure, an unprecedented economic development opportunity.

Table 3. Top 10 Countries with Technically Recoverable Shale Gas Resources

Rank	Country	Shale gas (trillion cubic feet)	
1	China	1,115	
2	Argentina	302	
3	Algeria	707	
4	U.S.[1]	665	(1,161)
5	Canada	573	
6	Mexico	545	
7	Australia	437	
8	South Africa	390	
9	Russia	285	
10	Brazil	24S	
	World Total	7,299	(7,795)

Source: US Energy Information Administration and Advanced Resources International

However, any region with a new source of shale gas condensate also has a new source of shale gas, and, hence, advantaged methane for C_1 derivatives as well. These new chemical industry centers could make a wide variety of products given a wet shale gas feedstock. Which processes and feedstock components to use will be an interesting technical competition and economic optimization. The catalyst innovations and process technologies that were previously developed when earlier feedstocks were advantaged or disadvantaged as discussed above all will be brought to bear. New innovations will also be developed, but not specifically because of the abundance of shale gas. The competition among C_1 and C_2 (and other) feedstock alternatives will continue unabated as it has in the past.

Methane (or carbon monoxide) and the olefins are two of the major basic feedstocks for the commodity organic chemicals industry. The other major feedstock are the aromatics (benzene, toluene and xylenes). Today, aromatics are almost totally produced by catalytic reforming in oil refineries.[48] One new opportunity that might arise specifically because of shale gas abundance in locations far removed from oil refineries is

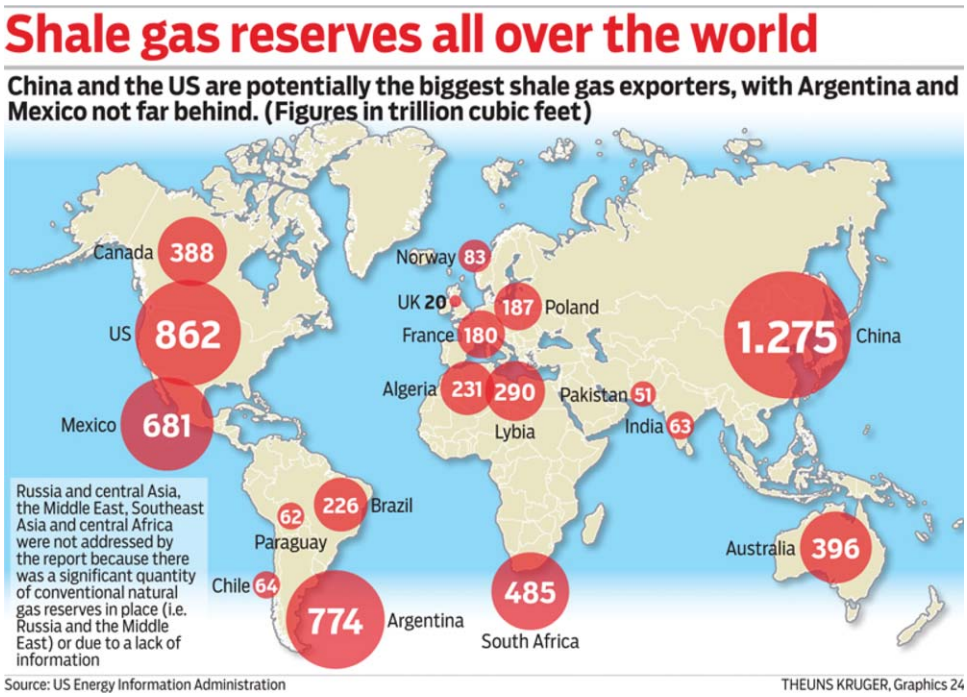


Figure 7. World shale gas reserves.

Source: US Energy Information Administration.

consideration of routes to aromatics from methane or ethane directly. Such processes have been proposed in the past, but so far the catalysts considered have had significant selectivity, coking, and lifetime issues.[49–51] However, the opportunity to create chemical processing centers in new geographic regions with all three major building blocks could be a large incentive for renewed catalyst and process development.

Outlook

Shale gas is a significant proportion of natural gas assets in the United States as well as in many other regions of the world. After considerable technological development, costs of production have proven to be competitive such that governments have reclassified shale gas and added it to technically recoverable natural gas reserves. There are some concerns related to potential adverse impacts of drilling through and contamination of near-surface aquifers, use and reclamation of water required for hydraulic fracturing, the fate of additives used in hydraulic fracturing fluids, seismic activity resulting from hydraulic fracturing, surface and habitat disruption because of roads, drilling pads, gathering pipelines, traffic, etc., during and after field development, and possible increased amounts of fugitive methane, itself a potent potential global warming gas. All of these concerns are being addressed by existing and developing regulations and better industry practices. Most believe that these concerns will be successfully managed.[52]

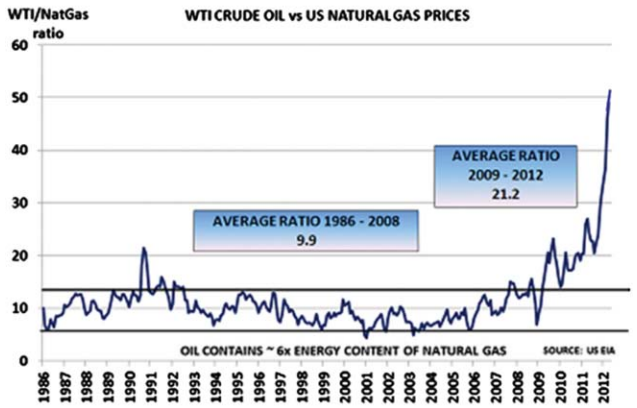


Figure 8. Ratio of Gas Price to Oil Price.

Source: ICIS.com.

Nevertheless it is recognized that there will be situations where shale gas development is not appropriate because of geological, surface use, economic, environmental, or other considerations. This is partly why estimates of recoverable shale gas are only a fraction (ca. one-quarter) of the total reserve thought to be in place. This fraction will likely change, in either direction, as more experience is gained. It is very possible that some areas are indeed too environmentally sensitive to develop, or that future production costs prove to be greater than early experience has suggested or that shale gas exploitation results in some unintended consequence not yet identified. It is also possible that through technological advances recovery fractions instead increase.

At this time it appears that shale gas development will have a significant world economic impact for at least several decades and possibly as long as a century or more. It is likely to accelerate the displacement of coal use for electrical

power production and in industrial boilers. In natural gas combined cycle configurations, electricity generation efficiency could be increased to a point that facilitates greater adoption of air- and ground-sourced heat pumps for domestic heating and of electric vehicles for transportation which could be two additional efficiency-based approaches to climate change mitigation (in addition to the option of carbon capture and sequestration from these stationary centralized gas combustion facilities).

At one point, the lower cost and greater supply of shale gas rekindled interest in gas-to-liquids fuels technologies to moderate crude oil import requirements. However, the simultaneous success of shale oil development appears to be a more capital-effective route to energy independence, and most GTL plans have been cancelled.[53]

For the chemical industry, it would appear that where it is plentifully available, shale gas will provide an economically advantaged feedstock and fuel for some time to come.[54]

Conclusions

The recent development of major new sources of shale gas methane and shale gas condensate will have many impacts on fuels and feedstocks in the United States and around the world. A much increased supply and expected stable, but advantaged cost will impact electric power production, may impact transportation, will impact first approaches to climate change mitigation, and should extend a healthy economically advantaged chemical processing industry and the beneficial products, services, and trade balance it provides. Because of regional shale gas and condensate availability, new chemical manufacturing facilities will be built. However, for the most part, the benefits of shale gas feedstocks are not contingent on new catalytic or process innovations, although such innovations will inevitably occur and may alter the preferred shale gas component for any particular application.

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